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Characterization of Pu Colloidal and Aqueous Species in Yucca Mountain Groundwater Surrogate

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Plutonium/Colloids/Speciation/Groundwater

Summary

The speciation and formation of Pu intrinsic colloids from an initial solution of Pu(V) were studied at pH 1, pH 3, pH 6, pH 8, and pH 11. The medium was a surrogate Yucca Mountain groundwater from well J-13 under air atmosphere. The solutions were monitored for several months. Samples were analyzed using liquid scintillation counting, ultra filtration, solvent extraction, photon correlation spectroscopy, and laser-induced photo-acoustic breakdown and emission spectroscopy. Redox potentials were measured periodically. The time dependencies of soluble and colloidal Pu concentrations are reported. The size and concentration of Pu colloid particles were estimated.

Introduction

Radionuclide speciation and groundwater composition are among the factors affecting the transport of radionuclides in groundwater. The migration of

radionuclide-bearing colloids is a potential mechanism for the release of actinides from an underground nuclear waste repository. Recent studies in Nevada revealed that a colloidal form of Pu was apparently transported over kilometer-scale distances through fractured volcanic rock on a timescale of decades [1]. It was not clear whether Pu was transported as an intrinsic Pu colloid or as Pu sorbed onto clay or zeolite particles.

Yucca Mountain remains a promising site for a geologic repository for nuclear waste containing plutonium. The dominant oxidation state of Pu in water at atmospheric oxygen fugacity Pu(V) [2]. In this work the behavior of Pu(V) in a surrogate Yucca Mountain groundwater from well J-13 under air atmosphere was studied at 25 °C and five different pH's (1, 3, 6, 8, and 11). The initial concentrations of Pu(V) were 10^{-4} M and 10^{-6} M.

Experimental Section

Reagent-grade chemicals from J.T. Baker, AR grade chemicals from Mallinckrodt, and deionized water from a Milli-Q2 purification system (>18 M Ω -cm) were used to prepare the J-13 surrogate and other aqueous solutions. The pH of the surrogate J-13 solutions was adjusted by adding HCl or NaOH in appropriate amounts.

Organic solutions for solvent extraction speciation were prepared by dissolving weighed amounts of 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one (PMBP), 99% purity and bis(2-ethylhexyl)-hydrogen phosphate (HDEHP), 97%

purity from Aldrich Chemical Co. in xylene, AR grade from Mallinckrodt and used without further purification.

The Pu oxidation state distribution was determined by solvent extraction as described in [3].

The plutonium used in this study was 99.84% (atomic) ^{242}Pu . It also contained 0.006% ^{238}Pu , 0.0005% ^{239}Pu , 0.109% ^{240}Pu , and 0.048% ^{241}Pu , determined by analysis of the material's alpha spectrum using the MultiGroup Analysis (MGA) code [4]. The ^{242}Pu stock solution was purified using anion exchange resin AG 1x8 in order to remove decay products and other impurities. A 98.6% pure Pu(V) stock solution was prepared by reduction of Pu(VI) at a platinum electrode in solution with pH 3 in an argon atmosphere using the EG&G Princeton Applied Research Model 264A Polarographic Analyzer/Stripping Voltammeter and associated equipment. The oxidation states of the Pu solutions were checked with the Model 260 Guided Wave Spectrometer and the alpha spectrum was analyzed by means of Model 7401VR Canberra Alpha Spectrometer. A Tri-Carb 2500TR scintillation counter manufactured by Packard Instrument Company was used for the determination of Pu.

The experiments were conducted in sealed 50 mL polycarbonate tubes under an air atmosphere. The initial volume of each Pu solution was 40 mL. A covered block heater was used to maintain the temperature at 25 ± 0.5 °C. Pu concentrations were determined using liquid scintillation counting, alpha spectrometry and MGA analysis. In general, Pu concentration measurements had

a standard deviation of $\pm 5\%$. The uncertainty interval was higher for solutions with very low Pu concentrations (10^{-8} M).

Ultra-Spin™ 400 microL capacity polyethersulfone ultrafilters with a pore size corresponding to a 100,000-Dalton molecular weight cut-off (0.01 micrometers) from Lida Manufacturing Corp. were used for centrifugal ultrafiltration of the Pu solutions. A series of the tests were conducted at all pH's used in the experiment to determine the Pu losses due to sorption during the ultrafiltration. Liquid scintillation counting results showed that at pH 1, pH 3, pH 8, and pH 11 the Pu activity losses were within the counting statistics error - less than 5%. The highest sorption was at pH 6 and amounted to 7% of the total Pu.

The colloid particle sizes, concentrations, and qualitative composition were evaluated by a MALVERN photon correlation spectroscopy (PCS) system, Model PCS 100/100A and a laser-induced photo-acoustic system using a Spectra Physics Nd:Yag laser, Model GCR-190. The emission spectrum of the breakdown plasma was recorded using an Action Research Corp. 0.3 m spectrograph, Model SpectraPro®-300i, a gated Andor Technology ICCD camera, Model DH520-25F-01, and associated optical components.

Results and Discussion

Ten Pu solutions were investigated. Solutions containing 10^{-4} M Pu(V) and 10^{-6} M Pu(V) were produced in J-13 surrogate at pH 1, 3, 6, 8, and 11, and Pu colloid formation has been monitored for seven months. The composition of the J-13 surrogate prior to pH adjustment and the addition of Pu is reported in Table 1.

Aliquots were taken from each tube periodically and analyzed by liquid scintillation spectrometry, PCS, and laser-induced photo-acoustic breakdown spectrometry. Three aliquots were taken at each sampling: non-shaken supernatant which represented the colloidal and dissolved fractions of Pu; non-shaken supernatant for ultrafiltration which represented just the dissolved (<0.01 micrometers) Pu; shaken solution which represented total Pu (colloidal, dissolved, and precipitated). The pH and redox potential of the solutions were measured periodically. Three or four times during the experiment a slight pH adjustment was required for the solutions with pH 6, 8, and 11.

The results for the concentration of dissolved Pu are shown in Figures 1 and 2. After seven months from the beginning of the experiment most of Pu in the 10^{-4} M solution was in the dissolved form at pH 1, 3, and 6. There was almost no dissolved Pu at pH 8; over 95 % of total Pu was in form of a precipitate. At pH 11, about 20% of Pu was in the dissolved form, 50 % was in colloidal form and 30% was a dense colloid or precipitate.

Results for the 10^{-6} M Pu solution are as follows: about 90% of Pu was in the dissolved form at pH 1, 3, and 6, about 80% at pH 8, the remainder of the Pu in these cases formed colloids and precipitate. At pH 11, 70% of Pu was in colloidal form and 30% was in the precipitate; essentially none was in the form of dissolved Pu.

The distribution of Pu oxidation states was determined by solvent extraction for the 10^{-4} M Pu and 10^{-6} M Pu concentration solutions after 34 and 39 days from the beginning of the experiment, respectively, and again after 174 and 175 days.

The distribution of Pu between different forms and oxidation states after 174 and 175 days is shown in Tables 2 and 3. For the 10^{-4} M Pu concentration set, the dominant species at pH 1 were Pu(VI) (21%), Pu(V) (20%), Pu(IV) (16%), Pu(III) (17%), and Pu polymer or colloid (24%); at pH 3 - Pu(V) (73%), and Pu polymer or colloid (18%); at pH 6 - Pu(V) (78%) and Pu polymer or colloid (16%); at pH 11 - Pu polymer or colloid (74%).

At pH 8 only ~4% of the total Pu was in solution in colloidal form, the rest of Pu (96%) was in precipitate (dense colloid or crystalline material).

For the 10^{-6} M Pu concentration set the dominant species' at pH 1 were Pu(V) (40%), Pu(VI) (15%), Pu(III) (12%), and Pu polymer or colloid (25%); at pH 3 - Pu(V) (71%), and Pu polymer or colloid (18%); at pH 6 - Pu(V) (64%) and Pu polymer or colloid (21%); at pH 8 - Pu(V) (59%) and Pu polymer or colloid (24%); at pH 11 - Pu colloid (81%).

For the characterization of the particle content, PCS, laser-induced photo-acoustic, and emission breakdown spectroscopies were used. The particle concentration was monitored over a period of eight months. Only at pH 11 was the particle concentration sufficiently high for the determination of the particle size distribution using PCS. Initially, a broad bimodal size distribution ranging from ~ 100 nm to ~ 800 nm, with peaks at 100 nm and 500 nm was observed for both Pu concentrations. However, after approximately two months, monomodal size distributions with a maximum at 100 nm (± 20 nm) were observed. These particle size distributions remained constant for the length of the experiment. In addition to the PCS measurements, the technique of laser-induced photo-acoustic

breakdown spectroscopy was applied to monitor the relative particle concentration of all samples. The breakdown probability (BDP) was measured as a function of the laser energy. A sigmoidal probability curve was fitted using the empirical function:

$$BDP = \frac{x^n}{k^n + x^n}$$

where x is the laser energy, mJ, k and n are empirical parameters.

The parameter k defines the laser energy that is necessary to obtain a 50% breakdown probability and is used to characterize the relative particle concentration of each sample. A typical measurement is depicted in figure 3 (pH 3, $C_{Pu}=10^{-4}$ M, 153 days).

The current setup of our laser-induced photo-acoustic breakdown spectroscopy system allows quantitative particle number determinations only for the case of monomodal size distributions. Due to the lack of this information for most samples, only a comparison of the particle concentrations is given in this report. Figure 3 shows the laser energy required to induce a breakdown probability of 50% for the samples at $C_{Pu}=10^{-6}$ M. The measurements indicate a decreasing particle concentration as a function of pH and time. For the 10^{-6} M solutions at pH 1 and 3, the particle concentration was below the detection limit after 61 days. Further experiments will be conducted until no further changes of the particle concentrations are detected. A detailed description of the theoretical background and the typical experimental setup of the laser-induced photo-acoustic spectroscopy can be found in the literature [5, 6].

The qualitative particle composition was determined by the measurement of the emission spectra of the breakdown plasma. For all samples the characteristic emission bands for K, Na, Ca and Mg were observed (Table 4 and figure 4). Although Pu colloids are present, Pu bands could not be observed due to the inefficient excitation from the breakdown-induced plasma.

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Table 1. Composition of J-13 surrogate.

Species	Anal. concentration, M	Chemical used
Na^+	2×10^{-3}	NaHCO_3
CO_3^{2-}	2×10^{-3}	NaHCO_3
SiO_2	1.07×10^{-3}	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$
Ca^{2+}	2.9×10^{-4}	$\text{Ca}(\text{OH})_2$
K^+	1.5×10^{-4}	KNO_3
NO_3^-	1.5×10^{-4}	KNO_3
Cl^-	1.9×10^{-4}	HCl , MgCl_2
Mg^{2+}	7.4×10^{-5}	MgCl_2
SO_4^{2-}	1.9×10^{-4}	H_2SO_4
F^-	1.1×10^{-4}	HF

Table 2. Distribution of Pu chemical forms for 10^{-4} M Pu after 174 days from beginning of experiment.

Species/pH	pH 1	pH 3	pH 6	pH 8	pH 11
Pu(IV)	16%	0%	0%	0%	0%
Pu(III)	17%	0%	0%	0%	0%
Pu(VI)	21%	1%	0%	0%	0%
Pu(V)	20%	73%	78%	0%	0%
Polymer	15%	11%	9%	0%	25%
Colloid	9%	7%	7%	4%	49%
Precipitate	1%	7%	4%	96%	24%

Table 3. Distribution of Pu chemical forms for 10^{-6} M Pu after 175 days from beginning of experiment.

Species/pH	pH 1	pH 3	pH 6	pH 8	pH 11
Pu(IV)	4%	1%	0%	2%	0%
Pu(III)	12%	3%	0%	4%	0%
Pu(VI)	15%	2%	5%	3%	0%
Pu(V)	40%	71%	64%	59%	0%
Polymer	23%	17%	13%	18%	0%
Colloid	2%	1%	8%	6%	81%
Precipitate	5%	5%	10%	8%	19%

Table 4. Observed laser-induced breakdown emission lines of particles suspended in J-13 surrogate at pH 8.

Emission wavelength, nm	Element
358.6	Mg I
393.8	Ca II
395.7	Ca II
404.3	K I
412.2	Na II
422.3	Ca I/II
588.9	Na I
765.9	K I
768.8	K I

CAPTIONS FOR THE FIGURES

FIGURE 1. Concentration of dissolved Pu in J-13 surrogate; initial Pu concentration - 10^{-4} M.

FIGURE 2. Concentration of dissolved Pu in J-13 surrogate; initial Pu concentration - 10^{-6} M.

FIGURE 3. Laser energy required to induce breakdown probability of 50% for 10^{-6} M Pu set as function of time and typical breakdown probability fit for one of samples (insert).

FIGURE 4. Raw breakdown emission spectrum of particles suspended in J-13 surrogate at pH 8, initial Pu concentration - 10^{-6} M, and fitted spectrum of same solution.

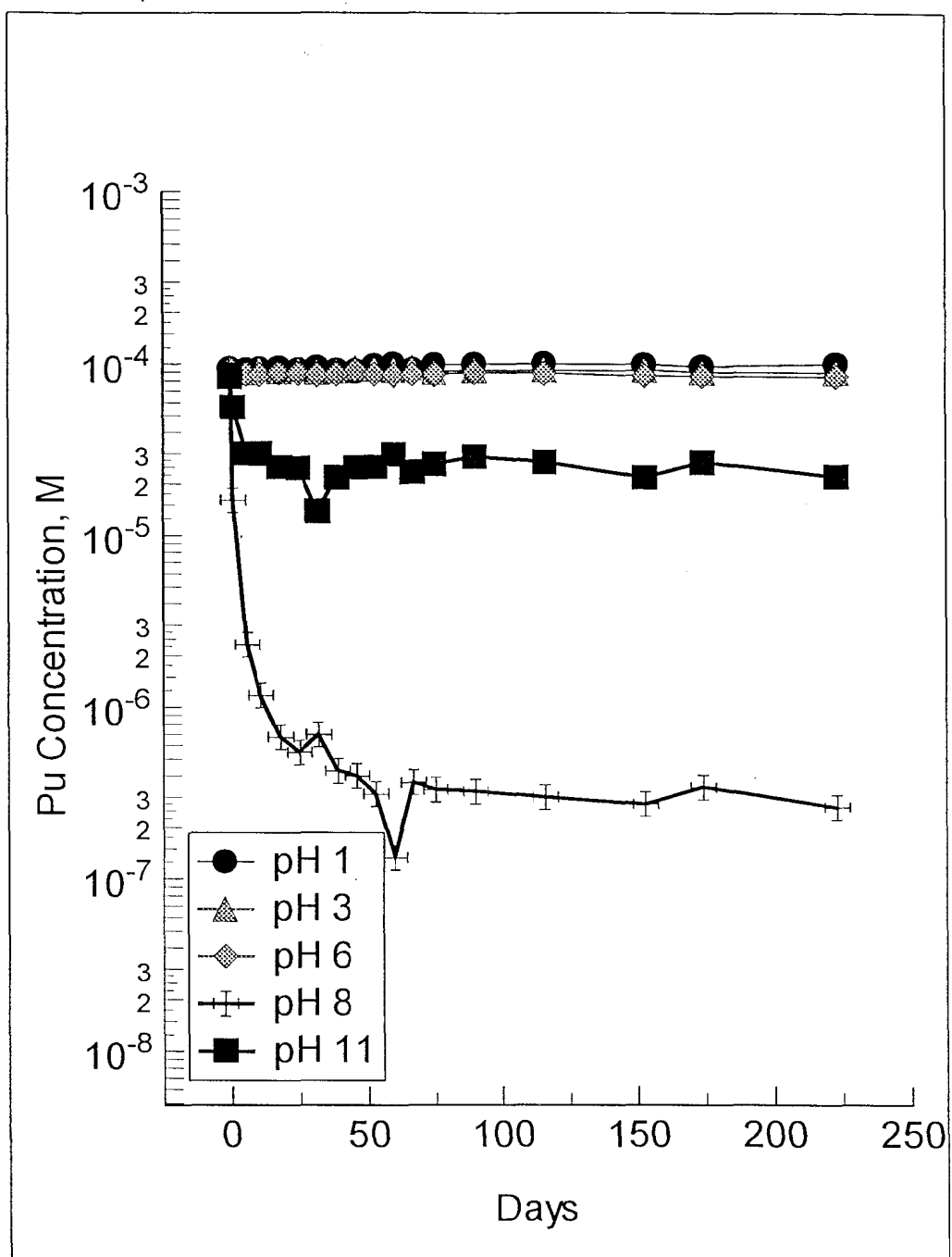


Figure 1. Concentration of dissolved Pu in J-13 surrogate; initial Pu concentration 10^{-4} M.

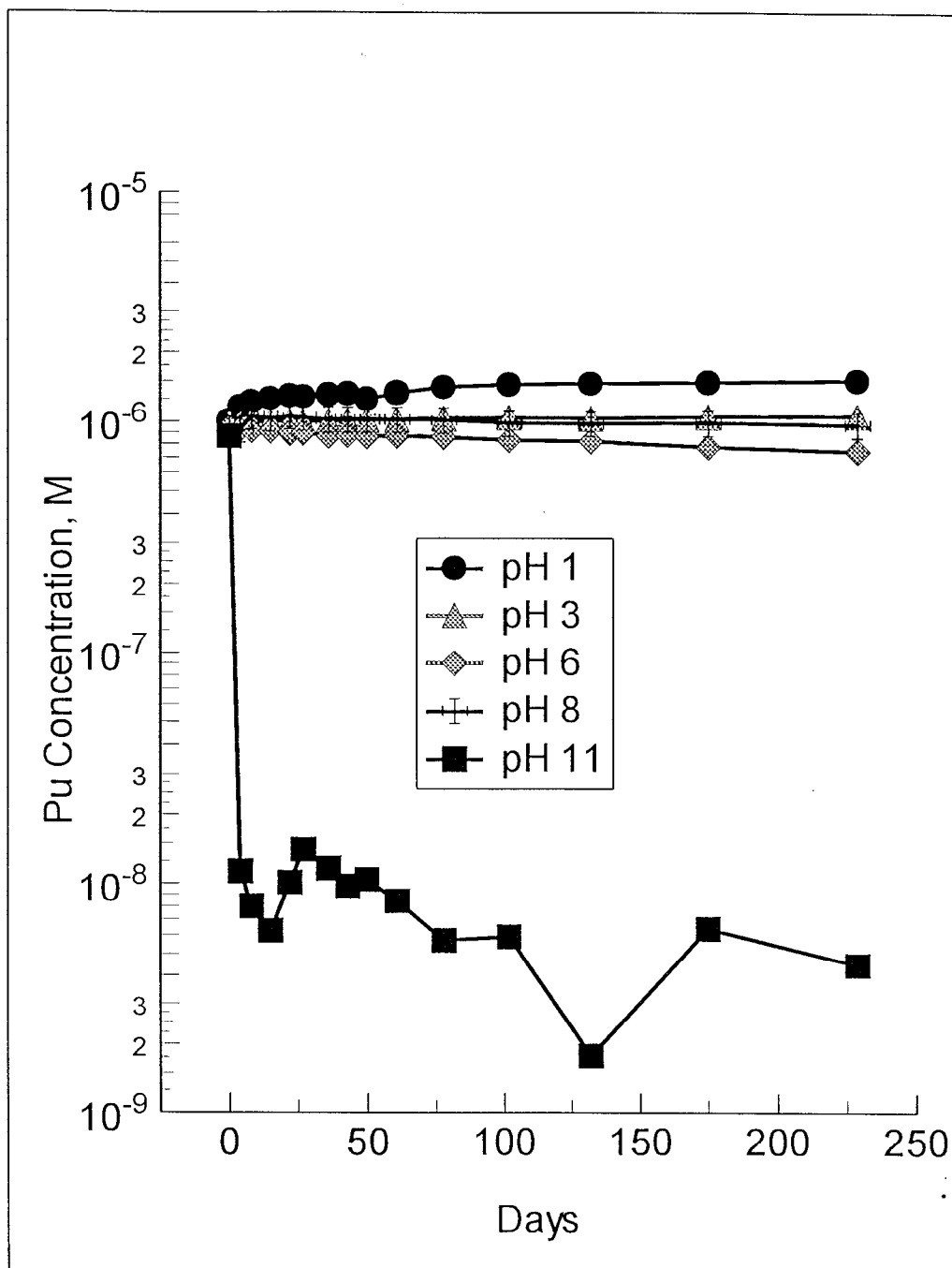


Figure 2. Concentration of dissolved Pu in J-13 surrogate; initial Pu concentration 10^{-6} M.

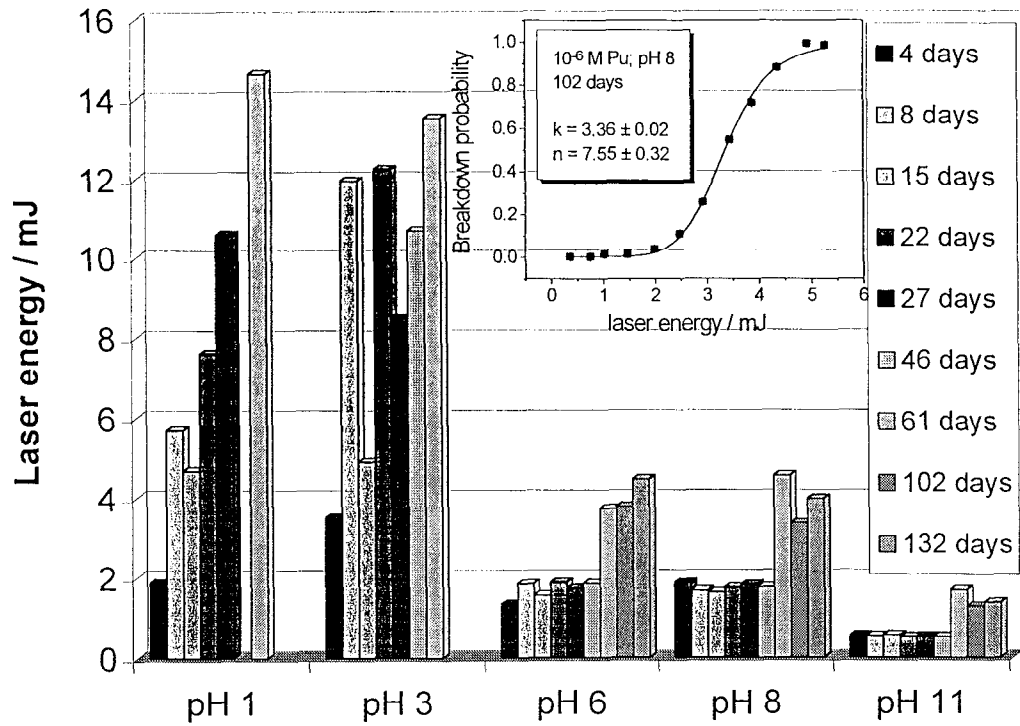


Figure 3. Laser energy required to induce breakdown probability of 50% for 10^{-6} M Pu set as function of time and typical breakdown probability fit for one of samples (insert).

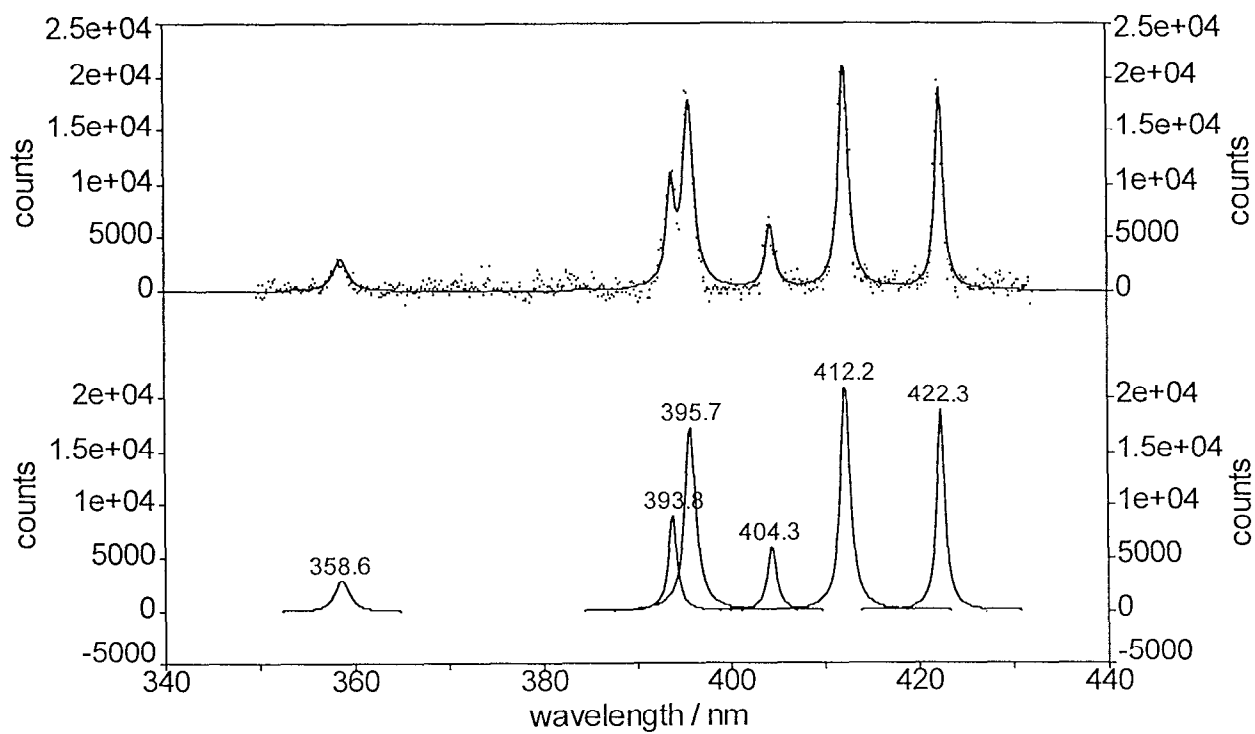


Figure 4. Raw breakdown emission spectrum of particles suspended in J-13 surrogate at pH 8, initial Pu concentration $\sim 10^{-6}$ M, and fitted spectrum of same solution.